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U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371

H-203691

U.S. APPLICATION NO. (If known, see 37 CFR 1.5

10/088427

INTERNATIONAL APPLICATION NO.  
PCT/US00/41149INTERNATIONAL FILING DATE  
12 OCT 2000PRIORITY DATE CLAIMED  
15 OCT 1999

TITLE OF INVENTION

GAS SENSOR DESIGN AND METHOD FOR USING THE SAME

APPLICANT(S) FOR DO/EO/US

DELPHI TECHNOLOGIES, INC/ DA YU WANG ET AL

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. ☐ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
  - a. ☐ is attached hereto (required only if not communicated by the International Bureau).
  - b. ☒ has been communicated by the International Bureau.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
  - a. ☐ is attached hereto.
  - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
  - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
  - b. ☐ have been communicated by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☒ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

## Items 11 to 20 below concern document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☐ A **FIRST** preliminary amendment.
14. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
15. ☐ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
18. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. ☐ Other items or information:

JC13 Rec'd PCT/PTO 15 MAR 2002

U.S. APPLICATION NO. 11,111,111, SEE 3 / 11,111,111

INTERNATIONAL APPLICATION NO.

ATTORNEY'S DOCKET NUMBER

10/088427

21. <input type="checkbox"/> The following fees are submitted: <b>BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):</b> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO. .... \$1040.00  International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO ..... \$890.00  International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO ..... \$740.00  International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) ..... \$710.00 International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) ..... \$100.00 <b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b>				CALCULATIONS PTO USE ONLY																					
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				\$ 890.00																					
<table border="1"> <thead> <tr> <th>CLAIMS</th> <th>NUMBER FILED</th> <th>NUMBER EXTRA</th> <th>RATE</th> </tr> </thead> <tbody> <tr> <td>Total claims</td> <td>33 - 20 =</td> <td>13</td> <td>x \$18.00</td> </tr> <tr> <td>Independent claims</td> <td>2 - 3 =</td> <td>- 0 -</td> <td>x \$84.00</td> </tr> <tr> <td colspan="3">MULTIPLE DEPENDENT CLAIM(S) (if applicable)</td> <td>+ \$280.00</td> </tr> <tr> <td colspan="3"><b>TOTAL OF ABOVE CALCULATIONS =</b></td> <td></td> </tr> </tbody> </table>				CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	Total claims	33 - 20 =	13	x \$18.00	Independent claims	2 - 3 =	- 0 -	x \$84.00	MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ \$280.00	<b>TOTAL OF ABOVE CALCULATIONS =</b>				\$ - 0 -	
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Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +				\$ - 0 -																					
<b>TOTAL FEES ENCLOSED =</b>				\$ 1,124.00																					
				Amount to be refunded: \$																					
				charged: \$																					

- a. ☐ A check in the amount of \$ \_\_\_\_\_ to cover the above fees is enclosed.
- b. ☒ Please charge my Deposit Account No. 50-0831 in the amount of \$ 1,124.00 to cover the above fees.  
A duplicate copy of this sheet is enclosed.
- c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 50-0831. A duplicate copy of this sheet is enclosed.
- d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

**NOTE:** Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

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NAME \_\_\_\_\_

35,844

REGISTRATION NUMBER

## GAS SENSOR DESIGN AND METHOD FOR USING THE SAME

This case claims the benefit of the filing date of the provisional application U.S. Provisional Application Serial No. 60/159,837 filed October 15, 1999, which is hereby incorporated by reference in its entirety.

5           This invention relates to gas sensors, and, more particularly, to  
oxygen sensors.

Oxygen sensors are used in a variety of applications that require qualitative and quantitative analysis of gases. In automotive applications, the direct relationship between the oxygen concentration in the exhaust gas and the air-to-fuel ratio of the fuel mixture supplied to the engine allows the oxygen sensor to provide oxygen concentration measurements for determination of optimum combustion conditions, maximization of fuel economy, and the management of exhaust emissions.

A conventional stoichiometric oxygen sensor typically comprises an ionically conductive solid electrolyte material, a porous electrode on the exterior surface of the electrolyte exposed to the exhaust gases with a porous protective overcoat, and an electrode on the interior surface of the sensor exposed to a known oxygen partial pressure. Sensors typically used in automotive applications use a yttria stabilized zirconia based electrochemical galvanic cell with platinum electrodes, which operate in potentiometric mode to detect the relative amounts of oxygen present in the exhaust of an automobile engine. When opposite surfaces of this galvanic cell are exposed to different oxygen partial pressures, an electromotive force is developed between the electrodes on the opposite surfaces of the zirconia wall, according to the Nernst equation:

$$E = \left( \frac{RT}{4F} \right) \ln \left( \frac{P_{O_2}^{ref}}{P_{O_2}} \right)$$

where:

- 5 E = electromotive force  
 R = universal gas constant  
 F = Faraday constant  
 T = absolute temperature of the gas  
 $P_{O_2}^{ref}$  = oxygen partial pressure of the reference gas  
 $P_{O_2}$  = oxygen partial pressure of the exhaust gas

10

Due to the large difference in oxygen partial pressure between fuel rich and fuel lean exhaust conditions, the electromotive force (emf) changes sharply at the stoichiometric point, giving rise to the characteristic switching behavior of these sensors. Consequently, these potentiometric oxygen sensors indicate qualitatively whether the engine is operating fuel-rich or fuel-lean, conditions without quantifying the actual air-to-fuel ratio of the exhaust mixture.

For example, an oxygen sensor, based on solid oxide electrolyte such as zirconia, measures the oxygen activity difference between an unknown gas and a known reference gas. Usually, the known gas is the atmosphere air while the unknown gas contains the oxygen with its equilibrium level to be determined. Typically, the sensor has a built in air channel which connects the reference electrode to the ambient air. To avoid contamination of the reference air by the unknown gas, the sensor requires expensive sensor package which usually has complex features in order to provide sufficient gas sealing between the reference air and the unknown gas. Historically, these gas sealed sensor packages have demonstrated insufficient durability in the field. This problem can be avoided by using in-situ electrochemical oxygen pumping. In this method, the air reference electrode chamber is replaced by a sealed reference electrode with oxygen electrochemically pumped in from the exhaust gas. This method eliminates the exhaust gas contamination problem but creates its own drawbacks. That is, an expensive electronic circuit is required to do the electrochemical oxygen pumping and excessive oxygen gas pressure built by the oxygen pump current can break open the sensor ceramic body.

What is needed in the art is a simplified gas sensor which employs a electrochemical pumping of oxygen.

# BRIEF SUMMARY OF THE INVENTION

5 A gas sensor and method for using the same. One embodiment of the gas sensor comprises: a first electrode and a reference electrode with an electrolyte disposed therebetween, wherein the first electrode and reference electrode are in ionic communication and a reference gas channel in fluid communication with the reference electrode and an exterior of the sensor, wherein  
10 the reference gas chamber has a diffusion limiter.

One embodiment of the method comprises: using a gas sensor comprising a first electrode and a reference electrode with an electrolyte disposed therebetween, wherein the first electrode and reference electrode are in ionic communication and a reference gas channel in fluid communication with the  
15 reference electrode and an exterior of the sensor; introducing an exhaust gas to the first electrode; applying a voltage to the reference electrode; ionizing oxygen at the first electrode; transferring the ionized oxygen across the electrolyte to the reference electrode; forming molecular oxygen at the reference electrode; ionizing the molecular oxygen on the reference electrode; transferring the ionized oxygen  
20 across the electrolyte to the first electrode to create a voltage; and measuring the voltage.

The above-described and other features and advantages of the present invention will be appreciated and understood by those skilled in the art from the following detailed description, drawings, and appended claims.

25

# BRIEF DESCRIPTION OF THE DRAWINGS

The apparatus and method will now be described by way of example, with reference to the accompanying drawing, which is meant to be exemplary, not limiting.

30

Figure 1 is an expanded view of a gas sensor design.

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Figure 2 is a graphical representation of exhaust flux measured from a gas-diffusion-limiting air channel against the leakage rates of the sensor package, the plateau of the data represents the limiting value of the exhaust flux.

Figure 3 is a graphical representation of limiting exhaust flux values against the width distribution (in percent (%)) of the air channels.

Figure 4 is an angled top view of one air channel design that has gas limiting means as well as gas buffering (storage) space to overcome oxygen pump problem related to the heater cyclic operation (heater on-off operation).

Figure 5 is an expanded view of alternative design of a gas sensor which has electrical isolation (ground isolation between the heater and the sensor emf) where the emf element and oxygen pump element are on the opposite side of the heater.

Figure 6 is an expanded view of alternative design of a gas sensor which has electrical isolation (ground isolation between the heater and the sensor emf) where the emf sensor and oxygen pump sensor are on the same side of the heater.

Figure 7 is an expanded view of an alternative gas sensor design with connection of the emf electrode leads and the heater leads outside of the sensor element level to further address the issue of isolation between emf electrode leads and the heater leads.

#### DETAILED DESCRIPTION OF THE INVENTION

The gas sensor comprises one or more electrochemical cells (i.e., an electrolyte disposed between two electrodes; an exhaust side electrode and a reference electrode), a porous protective layer disposed adjacent to the outer electrode, a reference gas chamber in fluid communication with the reference electrode, and a heater in thermal communication with the electrochemical cell. The reference gas chamber is additionally in fluid communication with the atmosphere around the gas sensor, i.e., the air and the exhaust gas. The reference chamber does not need to be hermetically sealed from the exhaust gas. The gas sensor avoids the requirement of hermetic sealing the reference gas chamber by pumping-in oxygen to the reference electrode and reference chamber thereby

creating a pressure gradient through the chamber. Optionally, one or more gas diffusion limiters may also be employed within the reference chamber.

Referring to Figure 1, the Nernst oxygen sensor is shown with the following basic features (components): exhaust side electrode 1, reference electrode 2, heater leads 3 and 4, porous protection layer 5, solid electrolyte layer 6, insulated alumina layers 7 and 8, air channel 9, and heater 12. In Figure 1, the exhaust gas electrode 1, is exposed to the exhaust gas through the porous protection layer 5. Reference electrode 2 is separated from exhaust electrode 1 by a dense solid electrolyte layer 6 and is exposed to the open channel 9 which is open to the ambient atmosphere at the tail 13 of the sensor. The heater leads 3 and 4 are connected to the positive and negative poles of a heater power supply 14, respectively. Optionally, the sensor can have the positive heater lead 3 connected to the reference electrode lead 17 through resistor R, and the heater negative lead 4 connected to the exhaust side lead 19. In this embodiment, there is a resistor R disposed between leads 3 and 17, thereby enabling the connections and the resistor to optionally be disposed inside the sensor ceramic body.

During use, the exhaust gas migrates to the electrode 1 through the protection coating layer 5 and generates an emf between exhaust electrode 1 and reference electrode 2. To keep reference electrode 2 at a constant oxygen activity, oxygen flux is pumped into electrode 2 by electric power supplied from heater lead 3 with a positive polarity maintained at the reference electrode 2. The oxygen generated at the reference electrode 2 will diffuse out of the reference gas channel 9 through the open end 13 into the ambient atmosphere (e.g., in to the exhaust gas or air).

25                    The diffusion rate out of the reference gas chamber 9/9' (see  
Figures 1 and 4) is linearly proportional to the difference of oxygen pressure  
between reference electrode (which is equal to or larger than about 1 atmosphere)  
and the ambient atmosphere (atm.) (which is equal to or smaller than about 0.21  
atmosphere). Because there is no gas diffusion limiting process employed in this  
30                    embodiment, the pressure of oxygen within the reference gas channel will never  
build up to a level to damage the ceramic sensor body. Meanwhile, the diffusion  
rate into the reference gas chamber by air and/or exhaust gas is linearly

proportional to the fuel concentration difference between the reference electrode (where the fuel concentration is kept at zero by the oxygen generated from the pump current) and the ambient atmosphere (which is typically about 21% or less). Since the fuel concentration difference doesn't exceed 21%, the exhaust flux is limited and can be described by Equation I:

$$F_{\text{exh}} = \frac{DCA}{L} \quad (I)$$

where:  $F_{\text{exh}}$  is the exhaust gas flux (i.e., the rate of exhaust gas migration through the channel)  
 D is the diffusion constant of exhaust gas constant  
 C is the ambient atm. exhaust gas concentration at the open end of the reference gas channel;  
 A is the average cross-sectional area of the gas channel; and  
 L is the length of the gas channel.

To keep the fuel concentration near zero at the reference electrode, the oxygen flux has to be larger than the limiting flux of the fuel. The amount of the oxygen flux is adjustable by the resistance value of R in Figure 1 and the heater voltage; wherein the amount of the limiting flux of the fuel is determined by the cross-sectional area and the length of the gas channel.

The gas sensor components, i.e., protective layer 5, electrodes 1, 2, 3, and 4 (and leads thereto), heater 12, dielectric layers 7 and 8, and heater supply 14. Furthermore, in addition to these conventional components, additional conventional components can be employed, including but not limited to additional protective coatings (e.g., spinel, alumina, magnesium aluminate, and the like, as well as combinations comprising at least one of the foregoing coatings), lead gettering layer(s), ground plane(s), support layer(s), additional electrochemical cell(s), and the like.

Dielectric layers 7 and 8 and any support layers typically comprise alumina or a similar material that is capable of inhibiting electrical communication and providing physical protection. Preferably, layers 7,8 as well as optional support layers are preferably capable of effectively protecting various portions of the gas sensor, provide structural integrity, separate various components, electrically isolate heater 12 from the sensor circuits, cover reference electrode 2,



heater 12, and/or lead(s), provide physical protection against abrasion, and/or electrically isolate the components of the gas sensor from the packaging.

Preferably, the materials employed in the manufacture of gas sensor comprise substantially similar coefficients of thermal expansion, shrinkage characteristics, and chemical compatibility in order to minimize, if not eliminate, delamination and other processing problems.

The dielectric, as well as support layers can each be up to about 200 microns thick, with a thickness of about 50 microns to about 200 microns preferred. These layers can be formed using ceramic tape casting methods or other methods such as plasma spray deposition techniques, screen printing, stenciling and others conventionally used in the art.

Disposed between two of the layers, e.g., 7 and 8 is heater 12, with a ground plane (not shown) optionally disposed between two support layers (not shown). Heater 12 can be any conventional heater capable of maintaining sensor end (i.e., end opposite open end 13) at a sufficient temperature to facilitate the various electrochemical reactions therein. Heater 12, which is platinum, alumina, palladium, and the like, as well as mixtures and alloys comprising at least one of the foregoing metals, or any other conventional heater, is generally screen printed onto a substrate to a thickness of about 5 microns to about 50 microns.

Leads 17 and 19 are disposed across various dielectric layers to electrically connect the external wiring of the gas sensor with electrodes 1, 2. Leads are typically formed on the same layer as the electrode to which they are in electrical communication and extend from the electrode to the terminal end of the gas sensor where they are in electrical communication with the corresponding via (not shown). Heater 12 also has leads 3 and 4 that are in electrical communication with vias.

In electrical communication with the leads are electrodes which are in ionic communication with the electrolyte. Electrolyte layer 6, 6', 6'', which is preferably a solid electrolyte that can comprise the entire layer or a portion thereof (see Figures 1, and 5 - 7), can be any material that is capable of permitting the electrochemical transfer of oxygen ions while inhibiting the physical passage of exhaust gases, has an ionic/total conductivity ratio of approximately unity, and is

compatible with the environment in which the gas sensor will be utilized (e.g., up to about 1,000°C). Also, this electrolyte can be formed via many conventional processes including, but not limited to, die pressing, roll compaction, stenciling and screen printing, tape casting techniques, and the like. Possible solid electrolyte materials can comprise any material conventionally employed as sensor electrolytes, including, but not limited to, zirconia which may optionally be stabilized with calcium, barium, yttrium, magnesium, aluminum, lanthanum, cesium, gadolinium, and the like, as well as combinations comprising at least one of the foregoing. For example, the electrolyte can be alumina and yttrium stabilized zirconia. Typically, the solid electrolyte has a thickness of up to about 500 microns, with a thickness of approximately 25 microns to about 500 microns preferred, and a thickness of about 50 microns to about 200 microns especially preferred.

It should be noted that, in some embodiments, a porous electrolyte may also be employed. The porous electrolyte should be capable of permitting the physical migration of exhaust gas and the electrochemical movement of oxygen ions, and should be compatible with the environment in which the gas sensor is utilized. Typically, porous electrolyte has a porosity of up to about 20%, with a median pore size of up to about 0.5 microns, or, alternatively, comprises a solid electrolyte having one or more holes, slits, or apertures therein, so as to enable the physical passage of exhaust gases. Commonly assigned U.S. Patent No. 5,762,737 to Bloink et al., which is hereby incorporated in its entirety by reference, further describes porous electrolytes that may be useful in the instant application. Possible porous electrolytes include those listed above for the solid electrolyte.

It should be noted that the electrolytes 6,6',6'' and protective material 5 can comprise entire layer or any portion thereof; e.g. they can form the layer, be attached to the layer (protective material/electrolyte abutting dielectric material), or disposed an opening in the layer (protective material/electrolyte can be an insert). The latter arrangement eliminates the use of excess electrolyte and protective material, and reduces the size of gas sensor by eliminating layers. Any shape can be used for the electrolyte and protective material, with the size and geometry of the various inserts, and therefore the corresponding openings, being

dependent upon the desired size and geometry of the adjacent electrodes. It is preferred that the openings, inserts, and electrodes have a substantially similar geometry.

The various electrodes 1, 2, 10, and 11 disposed in contact with electrolyte 6,6',6'' (see Figures 1, and 5 - 7) and porous electrolyte can comprise any catalyst capable of ionizing oxygen, including, but not limited to, metals such as platinum, palladium, osmium, rhodium, iridium, gold, and ruthenium; metal oxides such as zirconia, yttria, ceria, calcia, alumina and the like; other materials, such as silicon, and the like; and mixtures and alloys comprising at least one of the foregoing catalysts.

Electrodes 1, 2, 10, and 11 can be formed using conventional techniques such as sputtering, chemical vapor deposition, screen printing, and stenciling, among others, with screen printing the electrodes onto appropriate tapes being preferred due to simplicity, economy, and compatibility with the subsequent co-fired process. For example, reference electrode 2 can be screen printed onto dielectric layer 7 or over the solid electrolyte 6, exhaust electrode 1 can be screen printed over solid electrolyte 6 or on protective layer 5. Electrode leads and vias in the dielectric and/or electrolyte layers (not shown) are typically formed simultaneously with electrodes.

Disposed in fluid communication with the reference electrode 2 is the reference gas channel 9,9' formed by depositing a carbon base material, i.e., a fugitive material such as carbon black, between reference electrode 2 and layer 7 such that upon processing the carbon burns out, and leaves a void. (See Figures 1 and 4) As is evident from Figure 4, the geometry of the reference chamber can be altered to accommodate the particular application. In this particular embodiment, the reference gas channel 9' comprises two diffusion paths 21 and 23, with two chambers 23 and 25. The length and cross-sectional area of the various compartments (21, 23, 25, and 27) of the reference gas channel 9' are determined based upon Equation I above and the exhaust flux. In this embodiment two chambers and two diffusion paths are employed to account for a cycling of the heater voltage. Essentially, when no voltage is applied to the heater, no voltage is applied to the electrodes to induce pumping into the reference gas channel. To

inhibit ambient atm. access to the reference electrode, the multi-stage diffusion channel is employed. Where the voltage employed for pumping is not cyclical, a single chamber and channel can be employed. Here, the channel and chamber can be the same or a different size, based upon Equation I and the voltages to be employed.

The oxygen pump current has to be larger than the fuel limiting current in order to move oxygen across the electrolyte into the reference gas channel. However, if the current is too large it can create additional polarization at electrolyte (ohmic drop) and at electrodes (electrode polarization) which will create error signal to the emf measurement, especially during the light off time of the sensor operation. Consequently, a pump current of about 30 milliamperes per square centimeter ( $\text{mA}/\text{cm}^2$ ) or less of the exhaust electrode area can be used, with about  $20 \text{ mA}/\text{cm}^2$  or less preferred, and about  $10 \text{ mA}/\text{cm}^2$  or less especially preferred. This requirement can be achieved for example by selecting the right resistance value of R (see Figure 1), depending on the heater voltage used. The resistor can be carbon or metal oxide type resistor or can be thick film type which can be screen printed on the sensor ceramic body. If the heater uses an alternating current (ac) power supply, a diode can optionally be added to the circuit (in series with R, see Figure 1).

Due to the fuel limiting current, the reference gas channel should have a physical dimension to attain a limiting exhaust gas flux of about 30 milliamperes per square centimeter ( $\text{mA}/\text{cm}^2$ ) of the electrode area or less, with about  $20 \text{ mA}/\text{cm}^2$  or less preferred, and about  $10 \text{ mA}/\text{cm}^2$  or less especially preferred. Since the various parameters are interrelated, various amounts can be employed, depending upon the particular design of the sensor. The design should be based upon a combination of the Equation I above, and Equation II:

$$I_p = \frac{V_h - V_{emf}}{R} \quad (II)$$

where:  $I_p$  is the pump current;  
 $V_h$  is the heater voltage;  
 $V_{emf}$  is the sensor emf; and  
 R is the resistance of the resistor.

The heater or any other power device may be the power source for oxygen pumping. If the heater is the source and is operating in a cyclic mode, there is a period of time when no oxygen pumping occurs. If such period of time lasts too long, oxygen can be depleted at the reference electrode. A buffer zone can add into the gas channel design to avoid such difficulties. (See Figures 4-6) In these Figures, the reference electrode sits adjacent a small chamber 25 and a large chamber 27 functions as the buffer zone with a short diffusion-limiting path 21 connecting to the small chamber and a long diffusion path 23 connecting to the tail of the gas sensor. Pumped-in oxygen will be stored in the buffered zone to sustain the reference electrode over the period of time when no oxygen is supplied. Such gas channel can be made by screen printing with fugitive materials such as graphite or carbon which can be burned off during the sintering step. Oxygen storage

materials can also optionally be added to all or a portion of the reference gas channel (e.g., to the entire channel, to one or more diffusion paths, to one or more chambers, or to any combination of these channel portions) to increase the effectiveness of its function. Such materials include metals such as platinum, rhodium, palladium, ruthenium, iridium, osmium, and the like; metal oxides such as cerium oxide and bismuth oxide, and the like; as well as other conventional oxygen storage materials, and mixtures and alloys comprising at least one of the foregoing materials. Commonly assigned application, Attorney Docket No. DP-300023, U.S. Application Serial No. 09/476,834 to Detwiler, filed January 3, 2000, which is hereby incorporated in its entirety by reference, further describes oxygen storage materials that may be useful in the instant application.

In an alternative embodiment, electric isolation can be established between the heater and the emf element by employing an additional isolated pair of electrodes to do the oxygen pumping. Possible ways to do so are illustrated in Figures 5 and 6. Figure 5 shows a symmetrical design. The sensor has two almost identical sensor layouts similar to the one shown in Figure 1 but put on opposite sides of the ceramic heater. One of the sensors has an opening reference gas channel with its two leads 3 and 4 connected to the heaters. The other sensor has a gas channel through the heater ceramic to expose one of its electrodes (2) to the oxygen generated by the pump electrodes 10 and 11 and measures emf by electrodes 1 and 2. Since electrodes 1, 2 are electrically isolated from electrodes 10 and 11, this sensor design has the feature of signal ground isolation. Also because of electrodes 1 and 2 are separated from electrodes 10 and 11, the maximum oxygen pump current is not limited to 30 mA/cm<sup>2</sup>. the hole through the ceramic heater can be made by mechanical punching, drilling on the green tapes before the thermal lamination step.

Figure 6 shows another possible design that can achieve the same signal isolation. This time the emf sensing electrodes 1 and 2 and the oxygen pump electrodes 10 and 11 are put on the same side of the heater. Electrical isolation layer (e.g., a dielectric layer) such as alumina is put in between the two solid electrolytes cladded between the electrodes. The two isolated electrolytes can be in the form of button or strip. The open reference gas channel connects

both electrodes 2 and 4. The two pairs of electrodes can be side by side or one after the other.

Still there is another way to improve the signal-noise isolation. We can take away the connection between electrodes 1 and 4 from sensor element level (see Figure 1) and reconnect at the control board level as shown in Figure 7. A resistance R2 will add to give the feature of virtual ground isolation. In comparison with the method shown in Figures 4(a) and 4(b), this scheme is simpler.

During use, exhaust electrode 1, electrolyte 6, and reference electrode 2 form both a pumping cell and a reference cell, which can operate, even simultaneously. Oxygen in the exhaust enters the pumping cell through protective layer 5 where a voltage applied across electrodes 1 and 2 cause oxygen on electrode 1 to be ionized and pumped to reference electrode 2. Then the oxygen is available to provide the reference gas to determine whether the exhaust gas at the exhaust electrode fuel rich (A/F is less than about 14.7 for a gas engine) or fuel lean (A/F is greater than about 14.7 for a gas engine).

The following example is merely intended to further illustrate an embodiment of the invention and not to limit the scope thereof.

#### EXAMPLE

Alumina and yttria doped zirconia were mixed with binders, plasticizers, and solvents and roll-milled into slurry as is conventional. The slurry was then casted into tapes by doctor blade tape casting methods.

Platinum inks and carbon inks were screen printed onto the tapes in the structure as shown in Figure 1 (electrodes 1, 4 were platinum and reference gas channel 9 was carbon). The print of the carbon channel 9 had a basic physical dimension of 49 mm L by 0.86mm W by 0.015mm H; with the W varied at 13%, 20%, 25%, 50% and 100% of the value shown here. The reference gas channel had openings at the tail end of the gas sensor.

The tapes were thermally laminated, cut and co-fired at 1,500°C for several hours and later packaged for final testing. Because the sensors were new

and hermetically sealed, various sizes of leak holes were made into the sensor packages so that exhaust gas could leak into the tail part of the sensors.

The sensors were then operated in hot rich engine operation conditions (e.g., 5.7 liter (l), eight valve (V8) engine at 2,700 revolutions per minute (rpm) and 70 kilopascals (kPa) exhaust pipe back-pressure, 10% rich from stoichiometric point (i.e., an A/F of about 13.2), and an exhaust temperature 850°C), the limiting exhaust gas flux measured in terms of electrical current was measured as a function of the leak rate (which was measured against air at room temperature with a vacuum pump).

The results which demonstrate the diffusion limiting effect of the air channel on the exhaust flux are shown in Figure 2, in which the fuel limiting current is plotted against the logarithmic leak rate (in cubic centimeters per second ( $\text{cm}^3/\text{sec}$ )) of the sensor package. The observed limiting current plateau is 5 micro-ampere (mA) which indicates the exhaust flux diffused into the reference gas channel has a limiting value irregardless of the amount to which the exhaust gas contaminated the ambient atmosphere.

If oxygen was pumped into the reference chamber (i.e., up to 1.5 volts (V) directly applied between the exhaust electrode and reference electrode), the reference gas channel doesn't break. In other words, in contrast to a sealed reference gas channel, the current reference gas channel can withstand oxygen being pumped in at a voltage up to and even exceeding about 1.5 V without cracking due to excessive internal oxygen pressure build-up. This proves the reference gas channel indeed has a one-way-gas-diffusion-limiting feature. It limits the exhaust flux but does not limit the flow of oxygen and build up the oxygen pressure at the reference electrode to the point of cracking.

Next, the fuel limiting flux was measured as a function of the width of the reference channel. The results are plotted in Figure 3, in which the limiting exhaust flux are plotted against the percentage change of the width of the reference channel. As can be seen in this Figure, the limiting exhaust flux is linearly proportional to the linear dimension of the reference gas channel.

Due to the design of the gas sensor and especially the reference gas channel, diffusion of exhaust gas or contaminated air toward the reference



electrode is inhibited. This, in conjunction with the electrochemical pump method, eliminates the requirement of hermetic seal sensor package and the oxygen-pressure-buildup problem, and eliminates the expensive power supply and electronic circuit. A further advantage of the sensor, is, when a co-fired  
5 embodiment is employed, the production is simplified due to the ability to use fugitive material in the formation of the reference gas channel.

While preferred embodiments have been shown and described, various modifications and substitutions may be made thereto without departing from the spirit and scope of the invention, including the use of the geometries  
10 taught herein in other conventional sensors. Accordingly, it is to be understood that the apparatus and method have been described by way of illustration only, and such illustrations and embodiments as have been disclosed herein are not to be construed as limiting to the claims.

We claim:

1. A gas sensor, comprising:  
a first electrode and a reference electrode with an electrolyte disposed therebetween, wherein the first electrode and reference electrode are in ionic communication; and  
5 a reference gas channel in fluid communication with the reference electrode and an exterior of the sensor, wherein the reference gas chamber has a diffusion limiter.
2. A gas sensor as in Claim 1, wherein the reference gas channel has a limiting exhaust flux of about  $30 \text{ mA/cm}^2$  or less of reference electrode area.
3. A gas sensor as in Claim 2, wherein the reference gas channel has a limiting exhaust flux of about  $20 \text{ mA/cm}^2$  or less of the reference electrode area.
4. A gas sensor as in Claim 3, wherein the reference gas channel has a limiting exhaust flux of about  $10 \text{ mA/cm}^2$  or less of the reference electrode area.

5. A gas sensor as in Claim 3, wherein the reference gas channel has a size determined by Equation (I):

$$F_{\text{exh}} = \frac{DCA}{L} \quad (\text{I})$$

5

where  $F_{\text{exh}}$  is the exhaust gas flux (i.e., the rate of exhaust gas migration through the channel);  $D$  is the diffusion constant of exhaust;  $C$  is the ambient atm. fuel concentration at the open end of the reference gas channel;  $A$  is the average cross-sectional area of the gas channel; and  $L$  is the length of the gas channel.

6. A gas sensor as in Claim 5, wherein design of the reference gas channel is further based upon Equation (II):

$$I_p = \frac{V_h \cdot V_{\text{emf}}}{R} \quad (\text{II})$$

5 where  $I_p$  is pump current;  $V_h$  is heater voltage;  $V_{\text{emf}}$  is sensor emf; and  $R$  is resistor resistance.

7. A gas sensor as in Claim 1, wherein the reference gas channel has a length of about 35 mm to about 65mm, a width of about 0.50 mm or less, and a height of about 0.05mm or less.

8. A gas sensor as in Claim 7, wherein the length is about 35mm to about 50mm, the width is about 0.30mm or less; and the height is about 0.025mm or less.

9. A gas sensor as in Claim 8, wherein the length is about 40mm to about 48mm, the width is about 0.13mm or less, and the height is about 0.015mm or less.

10. A gas sensor as in Claim 1, wherein the reference gas channel further comprises an oxygen storage material.

11. A gas sensor as in Claim 10, wherein the oxygen storage material is selected from the group consisting of platinum, rhodium, palladium, ruthenium, iridium, osmium, cerium oxide, bismuth oxide, and mixtures and alloys comprising at least one of the foregoing materials.

12. A gas sensor as in Claim 1, wherein the reference gas channel further comprises a first chamber disposed adjacent to the reference electrode, wherein the first chamber has a cross-sectional area greater than a diffusion limiter cross-sectional area.

13. A gas sensor as in Claim 12, wherein the reference gas channel further comprises a second chamber further comprises a second chamber and a second diffusion path, wherein the second chamber is disposed in fluid communication with the first chamber, with the first diffusion path disposed therebetween, and the second diffusion path is disposed in fluid communication with the first diffusion path, with the second chamber disposed therebetween, and the second chamber has a cross-sectional area greater than the first chamber cross-sectional area and the second diffusion path has a cross-sectional area smaller than the first chamber cross-sectional area.

14. A gas sensor as in Claim 1, wherein the sensor further comprises a heater and a resistor, wherein the resistor is connected to a positive heater lead and to the reference electrode.

15. A gas sensor as in Claim 1, further comprising co-firing the sensor.

16. A method for operating a gas sensor, comprising:  
using a gas sensor, the sensor comprising a first electrode and a  
reference electrode with an electrolyte disposed therebetween, wherein the first  
electrode and reference electrode are in ionic communication, and a reference gas  
channel in fluid communication with the reference electrode and an exterior of the  
5 sensor;  
introducing an exhaust gas to the first electrode;  
applying a voltage to the reference electrode;  
ionizing oxygen at the first electrode;  
transferring the ionized oxygen across the electrolyte to the  
10 reference electrode;  
forming molecular oxygen at the reference electrode;  
ionizing the molecular oxygen on the reference electrode;  
transferring the ionized oxygen across the electrolyte to the first  
electrode to create a voltage; and  
15 measuring the voltage.

17. The method for operating a gas sensor as in Claim 16,  
wherein the reference gas channel further comprises a diffusion limiter.

18. The method for operating a gas sensor as in Claim 16,  
wherein the reference gas channel has a limiting exhaust flux of about  $30 \text{ mA/cm}^2$   
or less of reference electrode area.

19. The method for operating a gas sensor as in Claim 18,  
wherein the reference gas channel has a limiting exhaust flux of about  $20 \text{ mA/cm}^2$   
or less of the reference electrode area.



25. The method for operating a gas sensor as in Claim 24, wherein the length is about 40mm to about 48mm, the width is about 0.13mm or less, and the height is about 0.015mm or less.

26. The method for operating a gas sensor as in Claim 16, wherein the reference gas channel further comprises an oxygen storage material.

27. The method for operating a gas sensor as in Claim 26, wherein the oxygen storage material is selected from the group consisting of platinum, rhodium, palladium, ruthenium, iridium, osmium, cerium oxide, bismuth oxide, and mixtures and alloys comprising at least one of the foregoing materials.

28. The method for operating a gas sensor as in Claim 16, wherein the reference gas channel further comprises a first chamber disposed adjacent to the reference electrode, wherein the first chamber has a cross-sectional area greater than a diffusion limiter cross-sectional area.

29. The method for operating a gas sensor as in Claim 29, wherein the reference gas channel further comprises a second chamber and a second diffusion path, wherein the second chamber is disposed in fluid communication with the first chamber, with the first diffusion path disposed therebetween, and the second diffusion path is disposed in fluid communication with the first diffusion path, with the second chamber disposed therebetween, and the second chamber has a cross-sectional area greater than the first chamber cross-sectional area and the second diffusion path has a cross-sectional area smaller than the first chamber cross-sectional area.

30. The method for operating a gas sensor as in Claim 29, further comprising a heater electrically connected to the reference electrode, wherein a voltage is cyclically applied to the heater.

32. The method for operating a gas sensor as in Claim 16, wherein the operations of ionizing oxygen at the first electrode, transferring the ionized oxygen across the electrolyte to the reference electrode, and forming molecular oxygen at the reference electrode, occur substantially simultaneously  
5 with the operations of ionizing the molecular oxygen on the reference electrode, and transferring the ionized oxygen across the electrolyte to the first electrode to create a voltage.

33. The method for operating a gas sensor as in Claim 16,  
10 wherein the gas sensor further comprises a heater, and wherein the sensor has been co-fired.



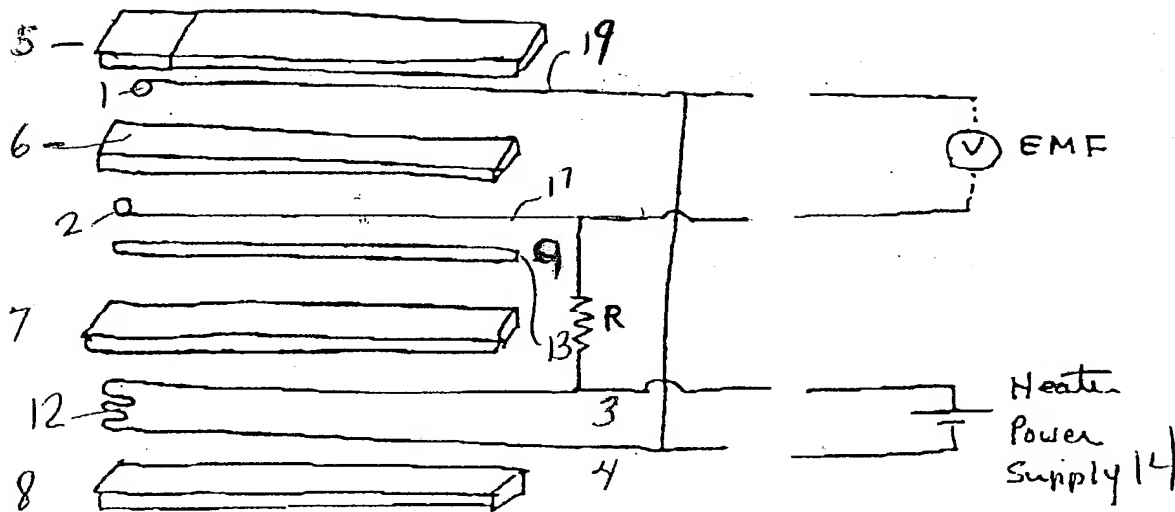
## GAS SENSOR DESIGN AND METHOD FOR USING THE SAME

### ABSTRACT OF THE DISCLOSURE

The gas sensor employs a reference gas channel which enables simultaneous or sequential pumping of oxygen and sensing of the exhaust gas (e.g., to determine if the exhaust gas is rich or lean). The method comprises: using a gas sensor comprising a first electrode and a reference electrode with an  
5 electrolyte disposed therebetween, wherein the first electrode and reference electrode are in ionic communication, and a reference gas channel in fluid communication with the reference electrode and an exterior of the sensor; introducing an exhaust gas to the first electrode; applying a voltage to the reference electrode; ionizing oxygen at the first electrode; transferring the ionized  
10 oxygen across the electrolyte to the reference electrode; forming molecular oxygen at the reference electrode; ionizing the molecular oxygen on the reference electrode; transferring the ionized oxygen across the electrolyte to the first electrode to create a voltage; and measuring the voltage.

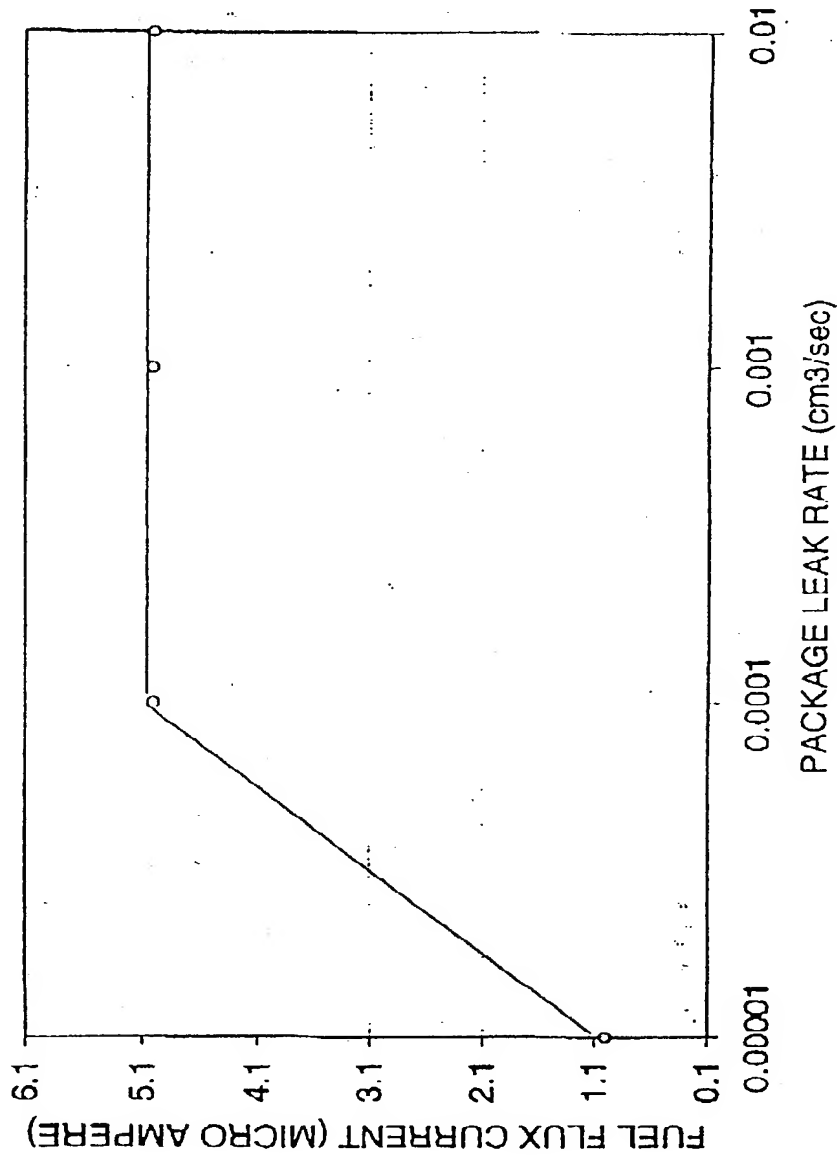
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Figure 1.



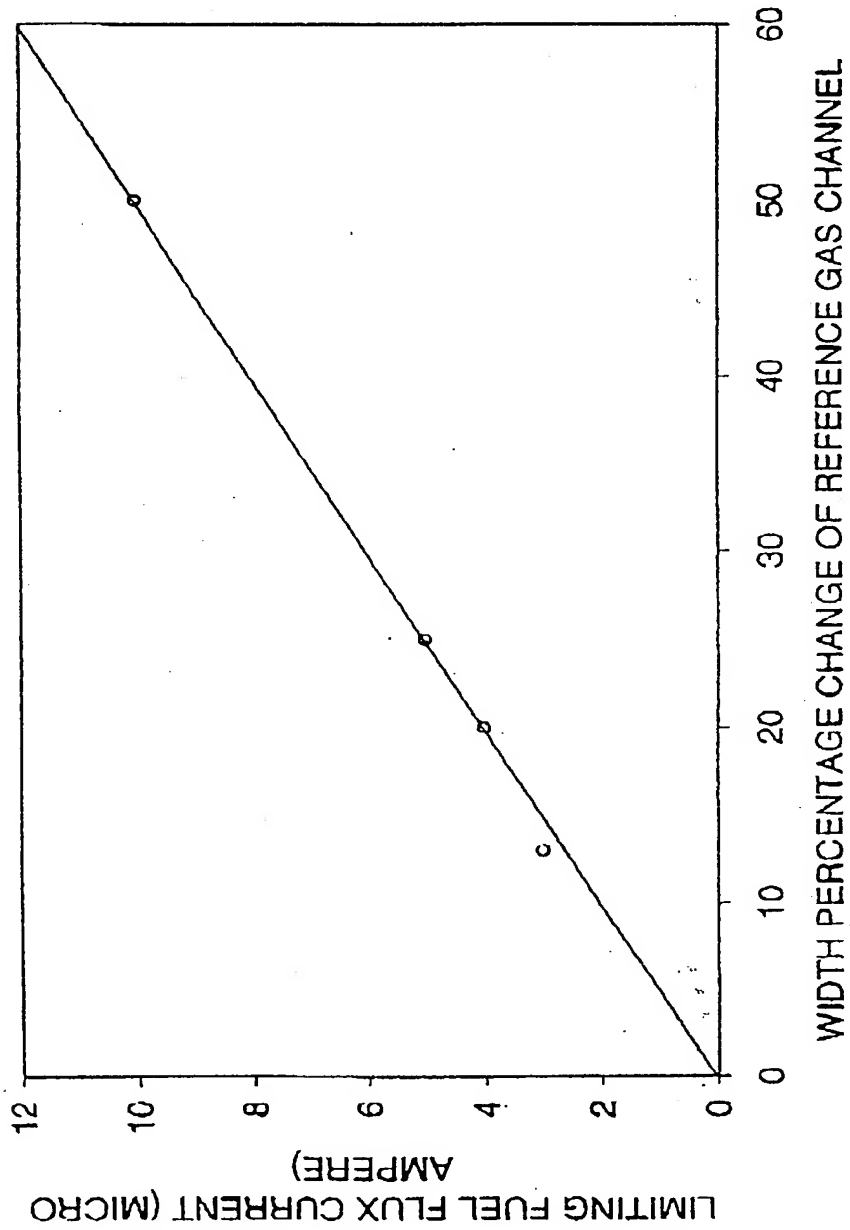
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Figure 2. Results of fuel flux as function of leak rate of package.



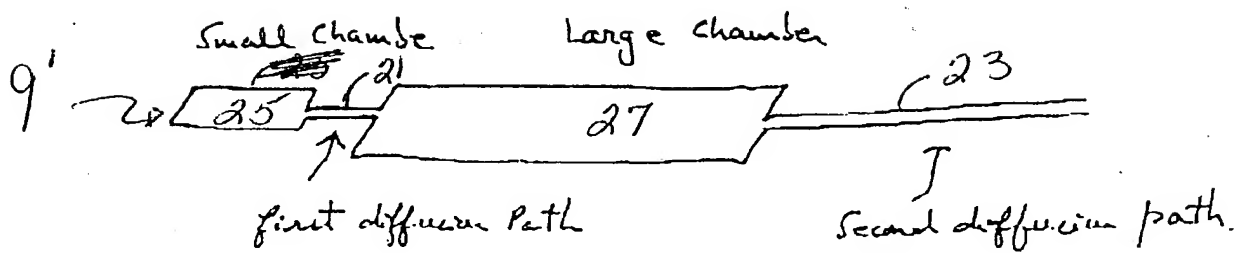
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FIGURE 3. Results of limiting fuel flux as function of reference channel width.



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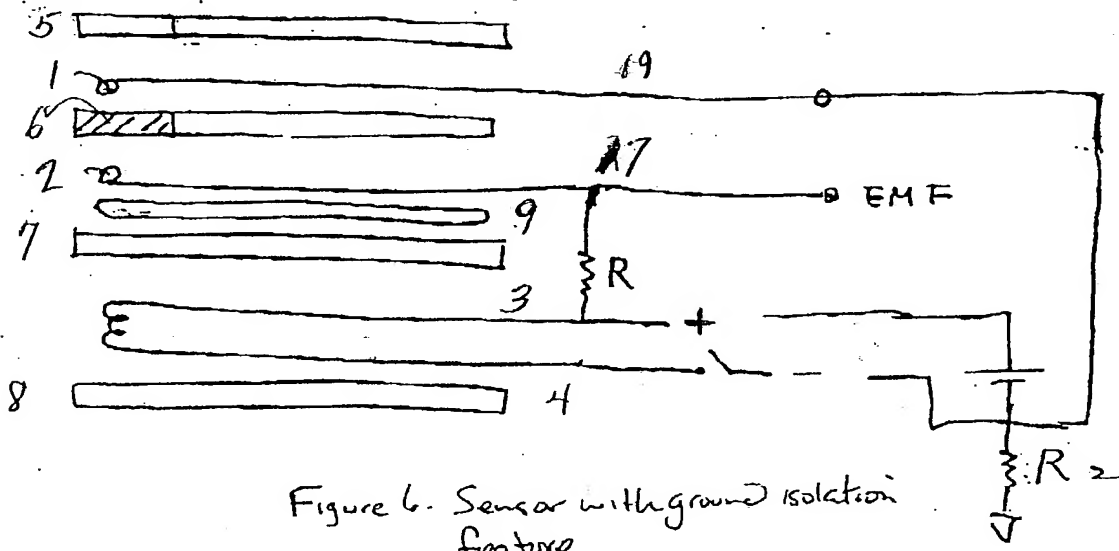
Figure 4. Layout of gas channel for heater cycling condition



Hand-drawn schematic diagram of a multi-tube heater circuit. The diagram shows seven horizontal tubes labeled 5, 6, 7-8, 10, 11, and 5 (bottom). Each tube has a pin labeled 19 or 17. A resistor R is connected between pins 9 and 11. A heater power supply is connected to pins 3 and 4. The diagram is labeled "Heater Power Supply".

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Figure 7. Sensor with ground isolation feature.



I hereby claim the benefit under 35 U.S.C. Section 119(e) of any United States provisional application(s) listed below:

60/159,837

October 15, 1999

(Application Serial No.)

(Filing Date)

(Application Serial No.)

(Filing Date)

(Application Serial No.)

(Filing Date)

I hereby claim the benefit under 35 U. S. C. Section 120 of any United States application(s), or Section 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. Section 112, I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, C. F. R., Section 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application:

(Application Serial No.)

(Filing Date)

(Status)  
(patented, pending, abandoned)

(Application Serial No.)

(Filing Date)

(Status)  
(patented, pending, abandoned)

(Application Serial No.)

(Filing Date)

(Status)  
(patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.





Docket No.  
H-203691 (DEP-0134F)

# Declaration and Power of Attorney For Patent Application

## English Language Declaration

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled  
**GAS SENSOR DESIGN AND METHOD FOR USING THE SAME**

the specification of which

(check one)

☐ is attached hereto.

☒ was filed on OCTOBER 12, 2000 as United States Application No. or PCT International Application Number PCT/US 00/41149 and was amended on \_\_\_\_\_

(if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, Section 119(a)-(d) or Section 365(b) of any foreign application(s) for patent or inventor's certificate, or Section 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate or PCT International application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application(s)

Priority Not Claimed

(Number)

(Country)

(Day/Month/Year Filed)

☐

(Number)

(Country)

(Day/Month/Year Filed)

☐

(Number)

(Country)

(Day/Month/Year Filed)

☐

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